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RESEARCH ON INDUSTRIAL WASTES AS RELATED TO WATER QUALITY

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Environmental Health Center
Cincinnati, Ohio

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RESEARCH ON INDUSTRIAL WASTES AS RELATED TO WATER QUALITY

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By

C. C. Ruchhoft, Sanitary Engineer Director

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It is the purpose of this paper to discuss industrial waste and water quality research that is needed to clarify the objectives for stream pollution abatement for the purpose of obtaining better water quality for domestic and industrial use. It is axiomatic that a bad tasting or smelling water is water of poor quality and is not conducive to public health, even though it is bacteriologically safe. The Public Health Service drinking water standards state:[1] "The water shall have no objectionable taste or odor." This requirement is included in the standard because public health authorities know that poor or unpleasant taste in an otherwise safe public supply drives the consumers to other water sources which may or may not be safe, or may cause consumers to reduce their water consumption below the requirement for good health.

Six years ago we[2] presented a paper on taste and odors in waters, and pointed out that the principal taste and odor contributing wastes included 1. Phenolic wastes, 2. Hydrocarbon or petroleum wastes, 3. Miscellaneous chemical wastes, and 4. Wastes from processing biological materials and/or biological processes. As far as the taste and odor contributing wastes are concerned, the situation has not changed materially since 1947. Although there has been an increase in industrial growth, the situation is more hopeful because concerted programs by pollution abatement and control agencies are now under way. The possibility of an eventual solution of these problems is also enhanced by the interest and cooperative attitude of industry. An excellent

pattern for an industrial waste cleanup program by industry is illustrated in a recent paper by Weston (3) of the Atlantic Refining Company. The activities of the committees from industry working with the Ohio River Valley Water Sanitation Commission in this area and the National Industrial Task Committee sponsored by the Public Health Service give promise of great progress on these problems.

Nevertheless, progress in the reduction of taste and odor producing constituents in surface water will be slow until additional research provides a better understanding and possible solution of these problems. This is because of the elusive nature of the critical constituents which contribute to the taste and odor characteristics. These materials usually are not contained in the suspended matter which can be removed by mechanical treatment. They are most frequently in true solution in low concentrations and are not readily attacked or removed by either chemical or biological oxidation processes. Consequently, when wastes containing such constituents are discharged into streams, they are not readily removed by natural self purification processes. Except for the phenolic compounds, their presence is not usually discovered by the analytical parameters of the ordinary stream pollution study and the actual nature of the constituents responsible for taste and odor usually remain unidentified after completion of even the most comprehensive stream study. In other words, there are almost no specific sensitive analytical tests for low concentrations of most of the large number of organic compounds that may be responsible for taste and odor in water supplies.

A recent report[4] points out that the diverse characteristics of the 89 different industrial effluents discharged into the Mersey River in the Manchester area of England makes ordinary standard tests valueless. There is a single organic chemical plant on the Ohio River system which has an industrial waste discharge that alone is so diverse that its effluents also cannot be successfully evaluated for pollutional constituents by standard tests.

Lamb and Jenkins[5] reported that synthetic organic chemicals are not attacked biochemically in the same way as sanitary sewage, and that in making B.O.D. tests, more than five days incubation may be necessary to estimate pollution loads. The conclusion of Lamb and Jenkins that B.O.D. should be run longer than five days illustrates the failure of the water pollution experts to recognise the need for new parameters of pollution evaluation. This is largely due to the fact that the water pollution control agencies demand data in terms of the old parameters regardless of their lack of significance in many situations. The significant conclusions from the Lamb and Jenkins study are that such synthetic organic chemical taste and odor producing effluents are more difficult to treat biologically than sewage and that they are also more persistent in streams.

It has also been pointed out previously[2, 6] that tastes and odors contributed by synthetic chemical manufacturers were not removed by normal self purification in streams, and that there were no satisfactory methods for the removal of such tastes and odors at water purification plants.

In view of the expanding chemical industry, it is imperative that the futility of trying to evaluate the pollutional effects of strong taste and odor producing constituents in such wastes by the old analytical techniques be understood. Much time and money can be saved if stream problems which involve only taste and odor difficulties in municipal supplies taken from the stream are not tackled by the old stream survey techniques. A more profitable program of study would include the following steps:

(1) The new concentration and chemical separation techniques (7, 8) should be used to isolate and separate the chemical groups of compounds, and identify the critical taste and odor producing constituents in wastes from the important industries that are involved.

(2) Sensitive methods of analyses for the detection and determination of the concentrations of such specific critical constituents with high threshold odor values must be developed.

(3) Studies to determine the persistence of these critical taste and odor producing constituents in surface waters should be made.

(4) Methods for removing such critical constituents below taste threshold values at the source and at water purification plants must be developed.

It must be understood that the solution of these problems can only be accomplished in a long range, intensive research program.

It cannot be accomplished in a few years by one small group such as ours at the Environmental Health Center. It will require the cooperative efforts of industry, including municipal and industrial water producers, pollution control agencies and university research groups to assure us better tasting water supplies from our surface waters in industrialized areas.

We at the Environmental Health Center have been working on a research program involving all phases of the above plan of attack for a number of years. A discussion of the progress being made on such studies has recently been presented (9) and need not be reviewed here.

To illustrate the complexity of this problem of taste and odor constituents, I would like to review for you some data obtained during a study of oil refinery gravity separator effluents. More complete data on this study on effluents from five refineries by the new concentration techniques will be given elsewhere (10). Briefly, the effluents under study are passed through a carbon filter assembly as shown in Figure 1. Facilities are provided to control the pH of the liquids passing through the filters. When a sufficient quantity of water has been passed through, the filters are taken down and the carbon is removed. The carbon is then air dried; after which it is extracted with a suitable organic solvent in large Soxhlet extractors. The extract is dried by appropriate means, and is then subjected to semi-systematic organic analyses based on differential solubilities, which has already been described in some detail (7,8,11).

The constituents of many wastes may better be concentrated by liquid-liquid extraction techniques (8). A typical apparatus for such an extractor is shown in Figure 2.

The quantity of organic materials extracted and the concentrations found by the carbon filter technique are shown for these refinery effluents in Table 1. It will be noted that the concentrations ranged from 7.5 to 87 p.p.m. and that gross quantities of extracts ranged from 17.4 to 369 grams, depending upon the quantity of effluent passed through the filter. Consequently, it is possible to obtain sufficient material for organic analysis by this procedure.

The composition of the organic compound groups found in the oil separator effluents is shown in Table 2. It will be noted that the neutral group of compounds, principally hydrocarbons, represents the greater proportion of all extracts obtained. These compounds represented from 57.5 to 87.4 percent of the total. The percentage composition for the other groups ranged from 0.6 to 24.7 percent for the phenolic group, from 0.2 to 11.1 percent for the acidic group, and from 0.33 to 4.5 percent for the basic group. The neutral group of compounds was further separated into five fractions by distillation.

The critical characteristics of these extracts as far as water supplies are concerned are taste and odor. The quantities of each of these constituent groups and of the total extract in parts per

billion required to give the odor threshold in water are shown in Table 3. The fact that it requires only 25 to 50 parts per billion of the extracts from refinery effluents to give the odor threshold shows the intense odor producing character of the waste. It will also be noted that the median quantities in parts per billion necessary to produce the odor threshold are 8 for the acidic group, 52 for the basic group, 90 for the phenolic group, and 26 for the neutral group. On the basis of the above median odor values for the groups, the quantities of each group present and the ease of biological attack of the different groups, it must be concluded that the neutral group is the most critical. Studies must be made on this group to devise methods for removing or reducing the odor constituents from the waste if relief from taste and odor characteristics is to be obtained in surface water supplies which receive such waste.

In most studies on secondary treatment of refinery waste reported to date reduction in B.O.D. has been the principal objective. In view of the composition of the waste as shown in Table 2, it is expected that B.O.D. would evaluate the phenolic group and partially the acid and basic groups in terms of oxygen requirement. Since most hydrocarbons are not readily oxidized in the ordinary B.O.D. test, the five day B.O.D. would not evaluate the neutral groups, which represent the greatest proportion of the critical constituents of this waste. Consequently, tests which evaluate also the neutral groups in petroleum waste must be used in evaluating the effectiveness of procedures for treatment of these wastes.

The new dichromate oxygen consumed test with silver sulphate catalyst (12) which is to be included in the new "Standard Methods" and which also is being considered by the American Society for Testing Materials should be an improvement over B.O.D. in evaluating the critical constituents of petroleum wastes. However, much work remains to be done by using both these tests on the petroleum constituents obtained by the concentration and separation techniques before an intelligent interpretation can be made of the results obtained by either test on these wastes.

The situation on the evaluation of critical constituents of other chemical wastes is just as confused as on petroleum wastes. Much research remains to be carried out on many other wastes to determine the critical constituents and objectives of treatment, and to evaluate testing methods and waste treatment procedures.

Water consumers have a very considerable interest in the solution of these problems. In this connection it is of interest to examine briefly the water quality situation for consumers of supplies on the Ohio River system. The difficulty of treatment and palatability of the finished water is usually related to the threshold odor concentrations and quality of the raw water. Figure 3 shows a plot of the monthly geometric mean threshold odor numbers for a number of points on the Ohio River system from September 1950 to July 1951.

It will be noted that Louisville has the lowest threshold odor number of all cities that are plotted on this chart. At Louisville, the values appear to be seasonal, and are highest in winter and lowest in summer.

At Weirton, West Virginia, about mile 930 from the mouth, the threshold odor number ranged from about 3 to 160. The highest values were obtained between September 1950 and February 1951. At Wheeling, West Virginia, about 30 miles downstream, in a highly industrialized area, the threshold odor numbers ranged from about 20 to 60, with a mean of about 30 for the entire period. Seasonal changes or water temperature seem to have little effect on the values observed at Wheeling.

The threshold odor values observed at Cincinnati generally range between 0 and 8, but occasionally higher values have been observed.

At Nitro, West Virginia, on the Kanawha River below the highly industrialized area of Charleston, very high threshold odors ranging between 60 and 600 were obtained. Recently, maximum threshold odor values up to 5000 were observed in the raw water at Nitro. The data for Nitro show that there is very little relief at any season from the high odor values that are attributable to wastes from chemical industries upstream.

We have periodically installed carbon filters at a number of water plants on the Ohio for the purpose of collecting and studying the organic extracts obtained from the water. The quantities of organic extracts obtained during a number of periods from the Cincinnati tap water in our laboratory are shown in table 4. These experiments covered the period from August 1950 to January 1951. Between 5,400 and 12,000 gallons of water were passed through the filters. It will be noted that during the period from December 27, 1950 to January 29, 1951, 11,640 gallons of water were passed through the filters at two pH values. At the normal pH, 4.56 grams of organics were obtained, while at a pH of 3.0 to 4.0, 10.88 grams of additional organics were obtained. During this period, these data indicate that 350 p.p.b. of organic constituents were being distributed to the consumers of Cincinnati. The values given in this table do not represent the exact quantities of materials contained in the water. We do not know the exact adsorption efficiencies for these unknown constituents on carbon. Neither do we know the elution efficiencies of these unknown mixtures and compounds from carbon with the organic solvents being used. Research to obtain some answers on these questions is under way. At present, all we can say is that the values given are certainly minimum values, and that somewhat higher concentrations of some constituents may be present. However, since the same carbon filter techniques were used at all sampling stations, the values for total organic constituents should be comparable.

That these extracts include constituents that contribute to the taste and odor problem is shown in Table 5. It will be noted that values from 3 to 25 p.p.b. of these extracts give detectable threshold odors in water. The data show that the concentrations of these extracts required to give odor to the water are of the same order of magnitude as the neutral compounds and phenolics, and of a lower order than the organic acids. The evidence is that all of these extracts are mixtures of many organic compounds. They have not been identified or even separated into groups at this time.

Because of our limited resources, it has not been possible for us to follow the content of organic compounds in water at many points. We have obtained more information at Nitro, West Virginia and Cincinnati than at other locations. The situation at Nitro is critical because of the high concentrations of these materials. Our studies indicate that the raw water at Nitro usually contains from 1 to 2 p.p.m. of these objectionable compounds. The municipal authorities at Nitro are unable to treat the raw water with all the facilities of a modern water plant to produce a satisfactory drinking water. They regularly use between 20 and 100 pounds of activated carbon per million gallons of water. They have used as much as 1000 pounds of activated carbon per million gallons. Our studies have indicated that this expensive treatment which is the best available to anyone at present will remove only about 50 percent of the constituents when the raw water contains 2.0 p.p.m. of these taste producing chemicals.

An infrared spectrogram for the extract from Nitro is shown in Figure 4. Because of the complexity of the extract, it is impossible to identify the compounds present. However, the absorption spectrogram does indicate the presence of compounds similar to the keryl benzenes, which are intermediates in the manufacture of wetting agents.

The maximum usefulness of the infrared spectrophotometric technique has not been obtained to date. This is because of the complexities of the mixtures present in the extracts from the wastes and waters, and the need for the further development of better separation and purification techniques applied to the organic extracts. The small quantities of extracts available from water supplies is another difficulty. However, our laboratory has just recently obtained a new and promising counter-current distribution apparatus. The use of this machine and the development of chromatographic techniques for use on fractions of the extracts should enable us to make better identifications with the infrared spectrophotometer.

If the data obtained at Nitro were unusual and unlikely to occur on other water sources, this situation would not be so serious. The fact that chemical industries producing obnoxious effluents and that the compounds producing tastes and odors in other water supplies on the Ohio have been increasing is indicated by our studies. A recent sample from Cincinnati showed an organic extract content of one part per million in the tap water which tasted and smelled bad. Our

present efforts are being directed toward the separation and group determination of the constituents in Cincinnati water. Infrared spectrograms and other tests of the raw water extracts of waters from different sources indicate that all of the extracts contain many compounds and suggest that there are very important differences in the constituents of the materials.

This problem needs a great deal of careful study, and it seems to be time for the water producers to undertake a study of the chemical characteristics of the materials contributing tastes and odors to their waters. Obviously, it will be a long time before the water pollution control agencies will be in a position to tell industries the objectives in waste treatment for removal of critical constituents that are not now identified. It also will be some time before industry will find the solution for the removal of many of these critical constituents. Consequently, it would seem highly desirable from the consumers' standpoint that experts in water treatment, that is, the municipalities and their consultants, study the chemical constituents in their raw material and the means for removal of these various objectionable taste and odor producing substances from the supplies before delivery to the consumers. This can be done by well directed research, on which the water production authorities should make major contributions.

Conclusion

In conclusion, it should be understood that the problems that are to be solved on the identification and treatment for removal of critical constituents in wastes from many industries can only be solved by well directed and objective studies on the part of the health and water pollution control agencies, the domestic water supply industry, chemical waste producing industries and other interested research groups. The water consumers have a large interest in the solution of these problems, and it is certainly important that the water producers determine the identity of the critical constituents in their sources of supply. It has been shown that chemical industries contribute wastes that contain critical taste and odor producing constituents that are not known.

The old chemical tests useful in stream studies where biochemical oxygen requirements are critical, are usually of little or no value in studying the abatement and control needs on these wastes. The newer concentration techniques that are applicable to such problems have been reviewed. Further research studies on phases of these problems that may be suggested follow.

(1) A study on the efficiency of the adsorption of organic chemicals from water on activated carbon and on the efficiency of recovery of these chemicals from the carbon by organic solvent extractions.

(2) A further study on the systematic separations of the organic extracts by the development and application of new physical and microchemical techniques.

(3) A study of the application of infrared absorption spectrophotometry to the identification of the constituent chemical groups and their persistence in surface waters.

(4) An intensive study of the identification of taste and odor producing constituents from all sources.

(5) A study of the chemistry of such constituents and the possibilities of physical, chemical, and biochemical breakdown of these constituents in surface waters.

(6) A study of all possible methods for the removal of various critical constituents in low concentrations from water sources.

Increasing understanding of the problems involved in improving water quality in water supply sources receiving discharges of industrial wastes and support of research toward solution of these problems will accelerate progress needed in the public interest.

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TABLE 1

RECOVERY OF ORGANIC MATERIALS FROM OIL SEPARATOR EFFLUENTS

BY CARBON FILTER TECHNIQUE

Refinery	Type of Prefilter(a)	Rate of Flow Gal/Sq Ft/Min	Depth of Carbon(b)	Quantity of Effluent Filtered(c)	Organic Material Recovered	
					Grams	PPM
A-1	Sand	3.0	24	7,500	369	13.0
2	Gran. Carbon	2.3	42	309	39.3	33.5
B-1	Sand	5.0	30	500	35.0	18.5
2	Sand	5.0	30	2,000	112	14.8
3	Gran. Carbon	2.5	48	500	137	72.0
C	Sand	4.2	18	2,080	59	7.5
D	Gran. Carbon	2.5	48	320	17.4	14.4
E	Sand	5.0	18	154	78.4	87.0

(a) Sand prefilters were not extracted. Granular carbon prefilters were extracted.

(b) In inches.

(c) In gallons.

TABLE 2

PERCENTAGE COMPOSITION OF THE ORGANIC EXTRACTS

FROM OIL SEPARATOR EFFLUENTS FROM

FOUR REFINERIES

Refinery	Neutral Group %	Phenolic Group %	Acidic Group %	Basic Group %	Loss %
A-1	84.5	3.7	0.15	0.44	11.2
2	78.5	4.5	1.0	1.00	15.0
B-1	57.5	24.7	1.9	1.4	10.9
2	85.0	1.3	0.5	4.4	9.1
3	85.0	4.2	0.2	0.4	9.3
C	87.5	0.6	0.2	4.5	7.2
E-1	64.0	1.1	0.9	0.33	33.0 (1)
2*	87.4	0.7	11.1		0.8

* This sample was obtained by liquid extraction. All others were obtained by carbon filter technique.

(1) This excessive loss is unaccounted for.

TABLE 3

THRESHOLD ODOR CONCENTRATIONS OF OIL SEPARATOR EFFLUENT EXTRACTS

Refinery	Threshold Odor Concentration — Parts per Billion (a)									
	Total Extract	Constituent Groups				Fractions of Neutral Group				
		Acidic	Basic	Phenolic	Neutral	1	2	3	4	5
A	25	0.14	14	28	25	11	17	16	9	220
B	37	8	86	90	40	-	-	-	-	-
C	32	32	18	98	19	16	23	15	20	-
B-1	28	4	112	54	26	9	10	19	26	840
B-2	52	14	-	225	49	-	36	27	92	6,700
Median Value	32	8	52	90	26	11	20	18	23	840

(a) Average obtained by 4 to 8 observers computed logarithmically.

TABLE 4

Recovery of Organic Extract from Cincinnati Tap Water Using Two Carbon Filters in Series under Alkaline and Acid Conditions

Series Number	Filter in Service From	Filter in Service To	Quantity Filtered (Gallons)	pH	Organic Material Extracted (grams)	Organic Material Extracted (P.P.b.)
1	8-10-50	8-29-50	5,400	8.5±0.3*	1.46	71
1a	8-10-50	8-29-50	5,400	3.0-4.0	1.39	68
2	10-26-50	12-7-50	12,096	8.5±0.3	3.25	71
2a	10-26-50	12-7-50	12,096	8.5±0.3	1.26	28
3	12-7-50	12-26-50	7,000	8.5±0.3	2.70	106
3a	12-7-50	12-26-50	7,000	3.0-4.0	3.0	113
4	12-27-50	1-29-51	11,640	8.5±0.3	4.56	103
4a	12-27-50	1-29-51	11,640	3.0-4.0	10.88	247
5	1-29-51	2-15-51	5,160	8.5±0.3	1.98	101
5a	1-29-51	2-15-51	5,160	3.0-4.0	1.42	72

* Usual range of pH of Cincinnati tap water.

TABLE 5

Lowest Concentration of Organic Extract Detectable by Water Dilution Method of Odor Testing

Source of Water*	Lowest Concentration Detected by Odor Test parts per billion
Huntington, W. Va.	13
Wheeling, W. Va.	25
Louisville, Ky.	13
Columbus, Ohio	3
Pomeroy, Ohio	6
Cincinnati, Ohio	25
A. Organic Groups:	
1. Phenolic	50
2. Neutral	11
3. Organic Acids	160

*All sources of water were filter effluents before chlorination except at Cincinnati where water treatment includes breakpoint chlorination.

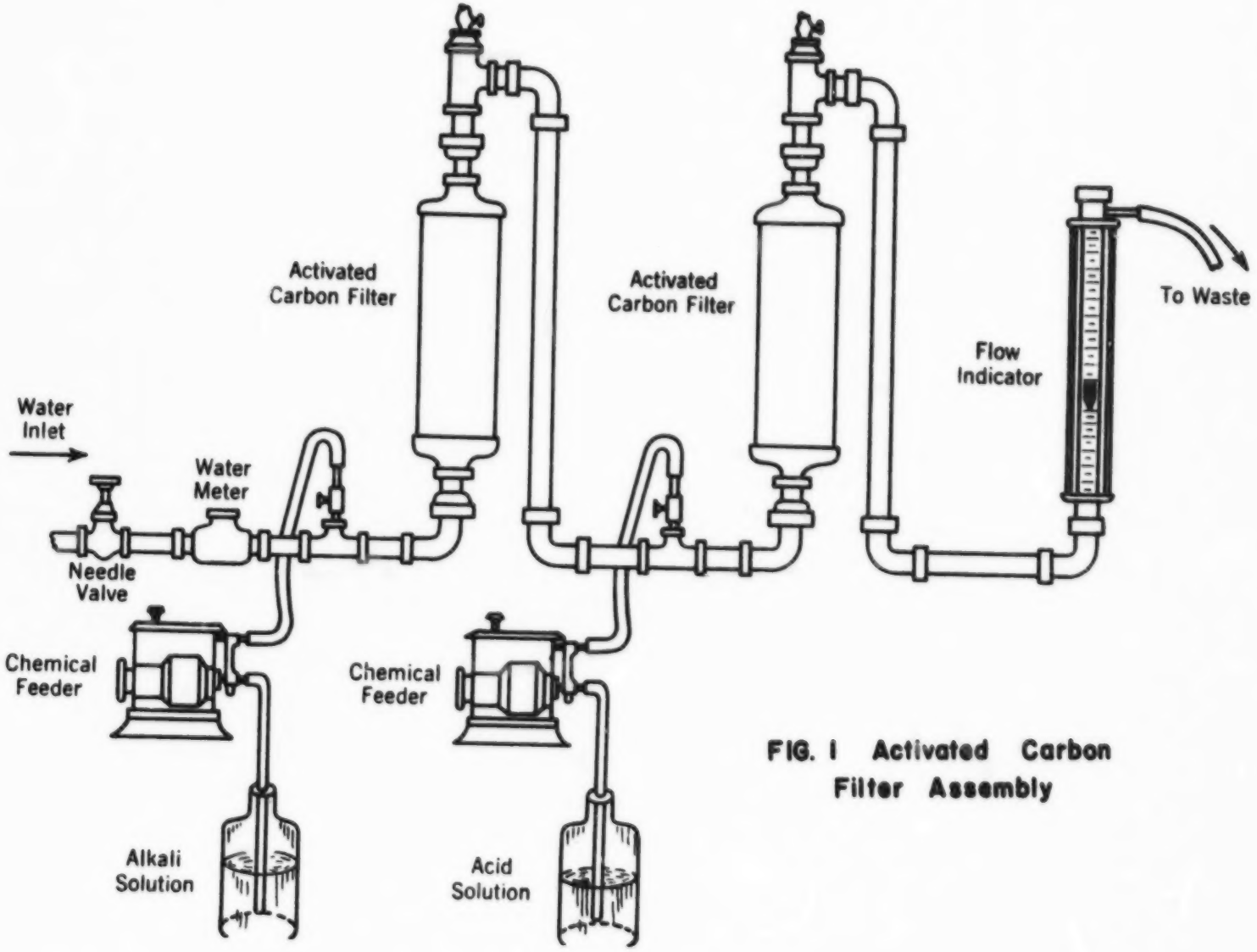
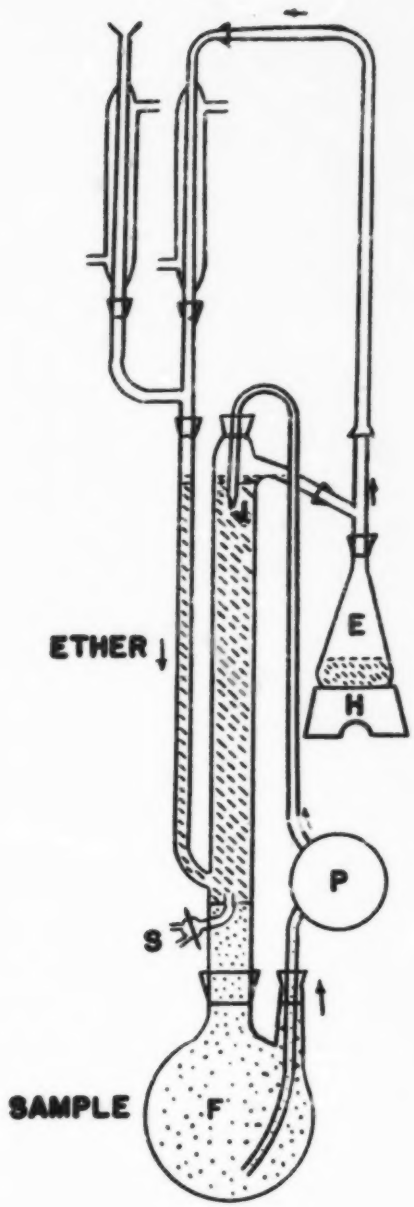


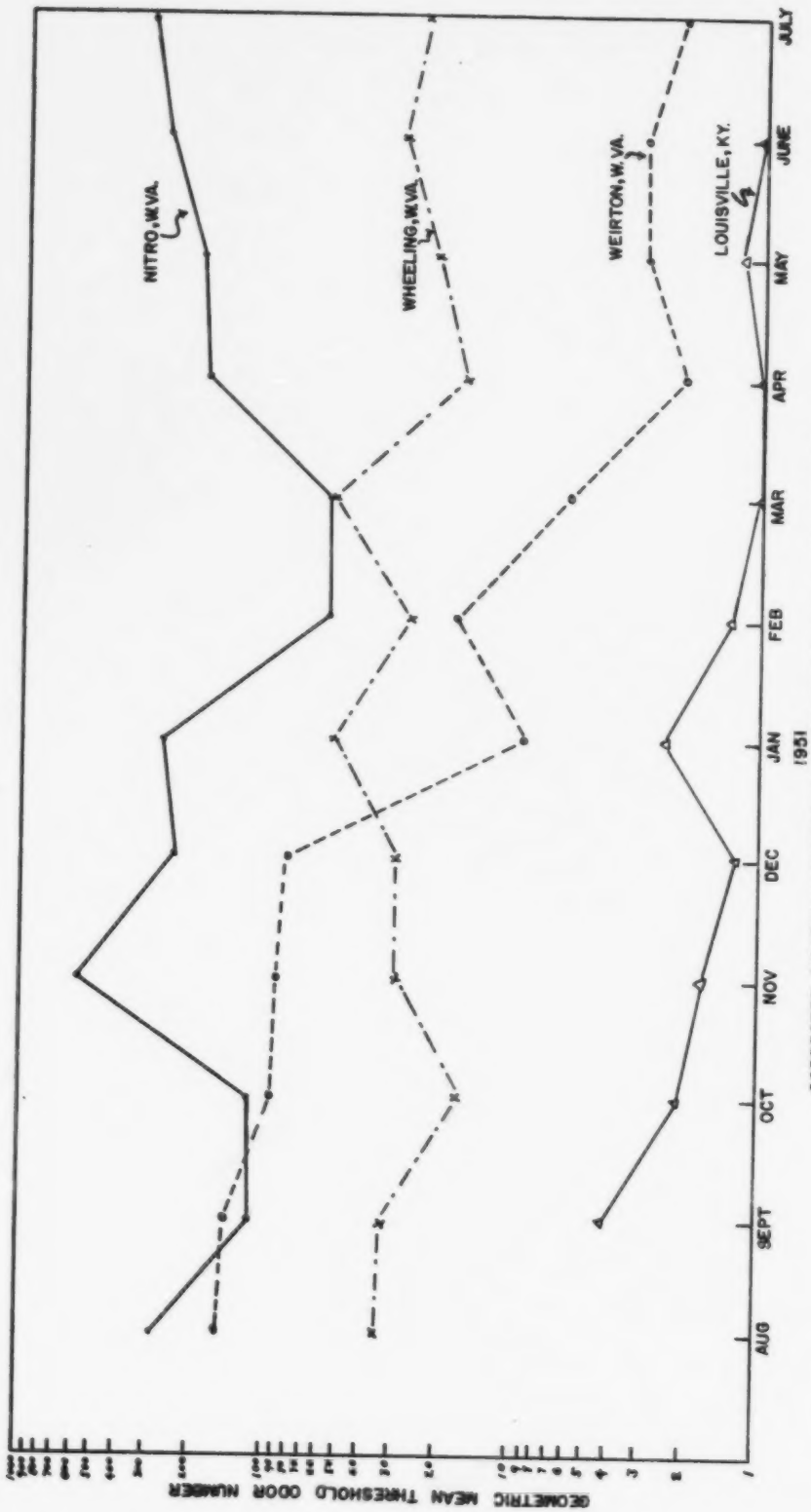
FIG. 1 Activated Carbon Filter Assembly



E- ETHER FLASK
F- SAMPLE FLASK
H- HEATER
J- JET TIP
S- 3-WAY STOP COCK
P- CIRCULATING PUMP

CONTINUOUS COUNTERCURRENT EXTRACTOR

FIGURE 2



CORRECTED MONTHLY GEOMETRIC MEAN THRESHOLD ODOR NUMBERS
RAW WATER
FIGURE 3.

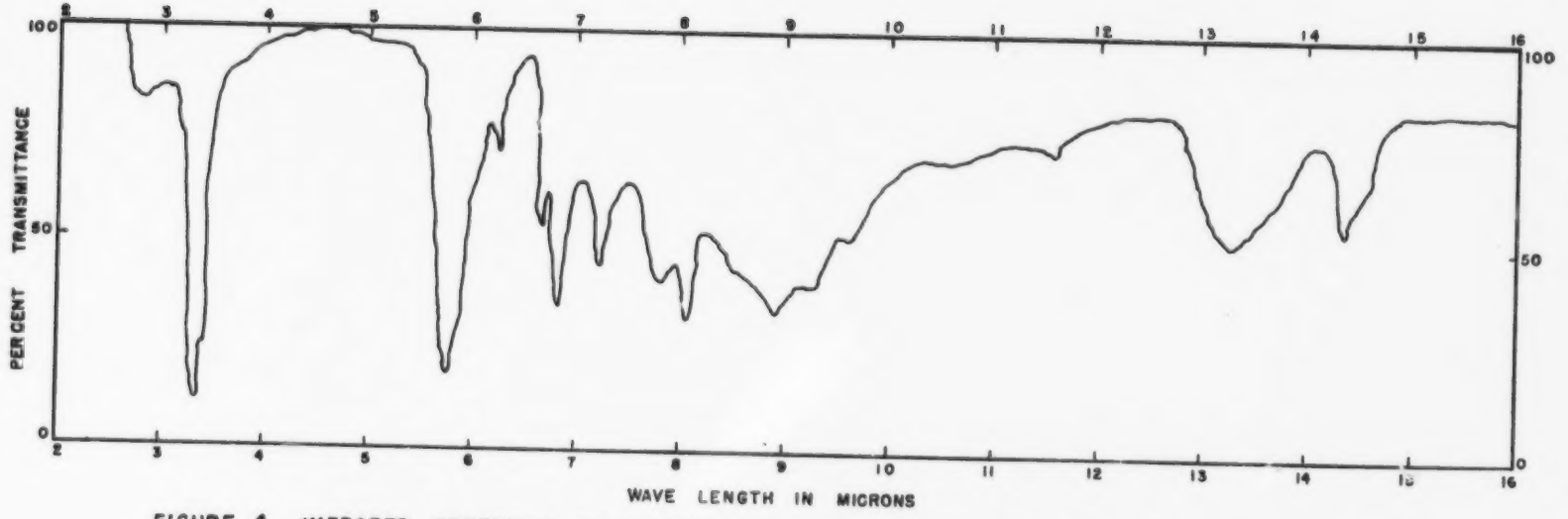


FIGURE 4. INFRARED SPECTRUM OF ORGANIC EXTRACT FROM NITRO, WEST VIRGINIA RAW WATER